Process for reducing the oxygen content of biomass using molybdenum-based catalysts

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$$A^{a+}{}_a(Mo_vX_xR^1{}_yR^2{}_zR^3{}_e)^{a*a-} \qquad (I)$$

(57) Abstract: The present invention concerns a process for converting biomass into useful organic building blocks for the chemical industry. The process involves the reduction of a polyol wherein at least two of the hydroxyl groups are located on adjacent carbon atoms in the presence of a molybdenum-based catalyst of the formula (I), such as $(NH_4)_6Mo_7O_{24}\cdot 4H_20$. A primary or secondary monohydric C1-C4 alcohol is used as reductant, as well as a solvent.

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PROCESS FOR REDUCING THE OXYGEN CONTENT OF BIOMASS USING MOLYBDENUM-BASED CATALYSTS

Field of the invention

The present invention concerns a process for converting biomass into useful building blocks for the chemical industry. The process involves the use of molybdenum-based catalysts, which are commercially available or may be readily prepared from industrial molybdenum compounds.

Background of the invention

The chemistry building blocks used in industrial polymers, fine chemicals etc. are typically prepared from fossil fuels. However, the use of fossil fuel-based building blocks is not sustainable, and it is therefore desirable to find alternative ways of preparing these building blocks.

Biomass and waste products from processes including biomass contain more oxygen than the products obtained from fossil resources, and they are therefore not immediately useful in preparing organic chemistry building blocks. One example of a waste product obtained from processing biomass is glycerol, which is a byproduct from biodiesel production. According to Ullmann's Encyclopedia of Industrial Chemicals, the production of glycerol will be six times higher than the demand by 2020. Glycerol is not useful as such as a building block, but if it is reduced to allyl alcohol, or even propylene, it could serve as a building block.

US 8,273,926 concerns a method for converting a polyol to the corresponding olefin by heating with formic acid. One of the polyols tested in this patent is glycerol. The disadvantages of the method include the need of carrying out three formic acid treatment/distillation/cooling-to-room-temperature cycles, the use of an inert atmosphere, and the separation of allyl alcohol from formic acid.

Yi et al., *ChemSusChem*, 2012, vol. 5, 1401–1404, describe rhenium-catalyzed deoxydehydration of glycerol, erythritol, and threitol. The authors also tested the catalytic activity of $(NH_4)_2MoO_4$ at 165 °C but were unable to isolate any products.

The disadvantage of using rhenium-based catalysts is the high and volatile price of the non-abundant metal.

Hills et al., *Eur. J. Inorg. Chem.*, 2013, 3352–3361, tested several molybdenum-based catalysts bearing rather complex acylpyrazolonate ligands in the deoxydehydration of 1-phenylethane-1,2-diol and 1,2-cyclooctanediol. They also tested two catalysts without the complex ligand (MoO_3 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in the deoxygenation of the reactive styrene oxide, but were unable to isolate any styrene. Styrene oxide is very different from typical biomass-derived polyols for several reasons. First of all, it is neither a diol nor a polyol but instead a much more reactive epoxide, which is furthermore activated in the benzylic position

DE 102008031828, US 5,616,817, US 2009/054701, EP 0415202, and Suprun et al. (Journal of Molecular Catalysis A, vol. 342, 91-100) all disclose the reduction of polyols using a catalyst that involves a minor amount of molybdenum. However, common to all these documents is that none of them disclose all the reactants being dissolved in the common reaction medium, and some of them are even concerning gas phase reaction. Furthermore, US 5,616,817 and EP 0415202 describe the reduction of the catalyst with hydrogen prior to reaction, meaning that the catalyst in question in fact contains metallic molybdenum.

Dethlefsen et al., *ChemSusChem*, 2014, 7, 425-428, disclose a process in an open system for converting polyols using molybdenum-based catalysts in the neat polyol or using a solvent which cannot be oxidized. Reductions in the neat polyols and/or the inert solvents have the disadvantage that the yield cannot exceed 50% of the starting polyols, due to the oxidation process that occurs in parallel to the deoxydehydration. When 1,5-pentanediol was employed as solvent, its dehydration and cyclization to tetrahydropyran was observed along with its disproportionation to *n*-pentanol and 3,4-dihydro-2*H*-pyran.

Shiramizu et al., Angewandte Chemie, vol. 51, p. 8082-8086, and Arceo et al., JACS vol. 132, p. 11408-11409, disclose the use of primary and secondary alcohols as reductant in a rhenium-catalyzed reaction with vicinal diols. Both these references disclose that higher alcohols lead to better results.

Hence, there exists a need for an improved process for reducing biomass and biomass-derived compounds in an efficient and cost-effective manner. Preferably, the process should involve a catalyst that is either already commercially available or is readily prepared from commercially available compounds.

Summary of the invention

Accordingly, the present invention concerns in one aspect a process for the reduction of a polyol wherein at least two of the hydroxyl groups are located on adjacent carbon atoms comprising the reaction of the polyol with a primary or secondary monohydric C_1-C_{10} alcohol in the presence of a molybdenum-based catalyst at a temperature of at least 175 °C, wherein said molybdenum-based catalyst has the formula:

$$A^{q+}{}_a(Mo_vX_xR^1{}_yR^2{}_zR^3{}_e)^{q*a-},$$

and wherein

A^{q+} is a mono-, di-, or trivalent counterion;

X is CO, O, OH, S, or Se;

R^1 is selected from the group consisting of H, F, Cl, Br, I, CN, N_3, NCS, dithiocarbamates, CH_3, BF_4, PF_6, SbF_6, and AsF_6;

R^2 is a mono-, bi- or tridentate ligand;

R^3 is a ligand coordinating to the central molybdenum atom through its π system selected from the group consisting of an alkene, a diene, a cyclopentadienyl, methylcyclopentadienyl, or pentamethylcyclopentadienyl radical, benzene, naphthalene, anthracene, or other aromatics;

a is 0, 1, 2, 3, 4, 5, or 6;

v is 1, 2, 3, 4, 5, 6, or 7;

x is in the range 2v to 6v;

y is 0, 1, 2, 3, 4, 5, 6, 7, or 8;

z is 0, 1, 2, or 3; and

e is 0, 1, 2, or 3,

wherein transition metals different from molybdenum are present in a molar amount less than the molar amount of molybdenum, and

wherein said polyol and said molybdenum-based catalyst are dissolved in said primary or secondary monohydric C_1-C_{10} alcohol or wherein said polyol, said molybdenum-based catalyst, and said primary or secondary monohydric C_1-C_{10} alcohol are dissolved in an additional solvent.

The process according to the invention uses a higher temperature than the processes disclosed by Yi et al. and Hills et al., who obtained no reduction product. It is therefore surprising that the present invention obtains high yields of reduction products using commercially available molybdenum-based catalysts.

Detailed disclosure of the invention

Definitions

In the present context, the term "primary or secondary monohydric C_1-C_{10} alcohol" is intended to mean a linear or branched hydrocarbon with one primary or secondary OH group and having 1 to 10 carbon atoms, such as methanol, ethanol, *n*-propanol, isopropyl alcohol, *n*-butanol, isobutyl alcohol, *sec*-butanol, *n*-pentanol, isopentyl alcohol, 2-pentanol, 3-pentanol, neopentyl alcohol, *n*-hexanol, isohexyl alcohol, and *n*-heptanol.

In the context of the present invention, the term "glycerol" is intended to mean the chemical compound $HOCH_2CHOHCH_2OH$, which is also commonly referred to as 1,2,3-trihydroxypropane or glycerin.

In the context of the present invention, the term "diol" is intended to mean an organic chemical compound containing two hydroxyl groups.

In the context of the present invention, the term "triol" is intended to mean an organic chemical compound containing three hydroxyl groups.

In the context of the present invention, the term "polyol" refers to a polyhydric alcohol, or polyalcohol, that is, an alcohol containing a plurality of hydroxyl groups, wherein at least two of the hydroxyl groups are located on adjacent carbon atoms.

In the context of the present invention, the term "sugar alcohol", also known as alditol, is intended to mean a reduced form of a carbohydrate where the carbonyl group (aldehyde or ketone) has been reduced to a primary or secondary hydroxyl group.

In the context of the present invention, the term "donor atom" is intended to mean the atom directly attached to the molybdenum atom. The term "monodentate ligand" is intended to mean a ligand having one donor atom. The term "bidentate ligand" is intended to mean a ligand having two donor atoms. The term "tridentate ligand" is intended to mean a ligand having three donor atoms.

In the context of the present invention, the term "transition metal" is intended to mean an element in groups 3 to 12 of the periodic table, including lanthanides and actinides. Thus, elements 21 thru 30 (Sc thru Zn), elements 39 thru 48 (Y thru Cd), elements 57 thru 80 (La thru Hg), and elements 89 thru 112 (Ac thru Cn) are considered transition metals in the context of the present invention.

In one aspect of the present invention, it concerns a process for the reduction of a polyol wherein at least two of the hydroxyl groups are located on adjacent carbon atoms comprising the reaction of the polyol with a primary or secondary monohydric C_1-C_{10} alcohol in the presence of a molybdenum-based catalyst at a temperature of at least 175 °C, wherein said molybdenum-based catalyst has the formula:

$$A^{q+}{}_a(Mo_vX_xR^1{}_yR^2{}_zR^3{}_e)^{q*a-},$$

and wherein

A^{q+} is a mono-, di-, or trivalent counterion;

X is CO, O, OH, S, or Se;

R^1 is selected from the group consisting of H, F, Cl, Br, I, CN, N_3, NCS, dithiocarbamates, CH_3, BF_4, PF_6, SbF_6, and AsF_6;

R^2 is a mono-, bi- or tridentate ligand;

R^3 is a ligand coordinating to the central molybdenum atom through its π system selected from the group consisting of an alkene, a diene, a cyclopentadienyl,

methylcyclopentadienyl, or pentamethylcyclopentadienyl radical, benzene, naphthalene, anthracene, or other aromatics;
a is 0, 1, 2, 3, 4, 5, or 6;
v is 1, 2, 3, 4, 5, 6, or 7;
x is in the range 2v to 6v;
y is 0, 1, 2, 3, 4, 5, 6, 7, or 8;
z is 0, 1, 2, or 3; and
e is 0, 1, 2, or 3,

wherein transition metals different from molybdenum are present in a molar amount less than the molar amount of molybdenum, and
wherein said polyol and said molybdenum-based catalyst are dissolved in said primary or secondary monohydric C_1-C_{10} alcohol or wherein said polyol, said molybdenum-based catalyst, and said primary or secondary monohydric C_1-C_{10} alcohol are dissolved in an additional solvent.

Temperature

As mentioned above, the temperature of the process of the present invention has been found to be an important parameter in obtaining a yield of reaction products. It has been found that the reaction temperature is advantageously at least 175 °C. There is in principle no upper limit on the reaction temperature, except for the critical point of the reaction mixture. However, it would be less than economical to run the reaction at a higher temperature than the temperature necessary to optimize the yield.

Accordingly, in one embodiment, the temperature is in the range 175 to 300 °C. In another embodiment, the temperature is in the range 190 to 290 °C. In yet another embodiment, the temperature is in the range 200 to 280 °C. In a further embodiment, the temperature is in the range 220 to 270 °C. In still a further embodiment, the temperature is in the range 230 to 260 °C.

Polyol

The process of the present invention achieves the reduction of biomass material or biomass-derived byproducts. Common to these biomass products is that they

are polyols in the meaning used in the present context. Biomass-derived material may contain larger molecules, such as macromolecules, wherein only parts of the molecule contain a plurality of hydroxyl groups. The present invention is also intended to encompass these molecules in the process.

The polyol can be cyclic or acyclic. In one embodiment of the invention, the polyol contains at least two hydroxyl groups located on adjacent carbon atoms, wherein both said hydroxyl groups are primary or secondary alcohol groups. In another embodiment, the polyol is a diol or triol. In a further embodiment, the polyol is selected from the group consisting of 1,2-hexanediol, 1,2-decanediol, and glycerol. In still a further embodiment, the polyol is a diol. In yet a further embodiment, the polyol is a triol.

In another embodiment of the invention, the diol is 1,2-propanediol, 1,2-butanediol, 1,2-pentanediol, 1,2-hexanediol, 3,4-hexanediol, 2-ethyl-1,2-butanediol, 3-ethyl-3,4-hexanediol, 2,3-dimethyl-2,3-butanediol, 1,2-octanediol, 1,2-decanediol, 1,2-dodecanediol, 1,2-tetradecanediol, *cis*-1,2-cyclooctanediol, *trans*-1,2-cyclooctanediol, *cis*-1,2-cyclohexanediol, *trans*-1,2-cyclohexanediol, *cis*-1,2-cyclopentanediol, *trans*-1,2-cyclopentanediol, 1,4-anhydroerythritol, or a mixture thereof.

In yet another embodiment of the invention, the triol is glycerol, 1,2,6-hexanetriol, 1,2,3-butanetriol, 1,2,3-hexanetriol, 1,2,3-cyclohexanetriol, or a mixture thereof.

An important byproduct in biodiesel production is glycerol. Hence, in still another embodiment, the polyol is glycerol.

In a further embodiment of the invention, the polyol is a sugar alcohol, monoanhydro sugar alcohol, sugar, or a mixture thereof. In yet a further embodiment of the invention, the polyol is xylitol, sorbitol, arabinitol, ribitol, mannitol, galactitol, iditol, erythritol, threitol, isomalt, lactitol, quinic acid, shikimic acid, or a mixture thereof. In still a further embodiment of the invention, the polyol is glucose, fructose, sucrose, lactose, maltose, xylose, or a mixture thereof.

Primary or secondary monohydric alcohol

A reduction reaction requires a reductant, which in turn is oxidized in the reaction. In addition, the reactants are preferably dissolved. It has been found that the primary and secondary monohydric alcohols used in the process of the invention serve both as reductants and as solvents for the polyols and the molybdenum-based catalyst. Hence, two advantageous properties are achieved with the primary and secondary monohydric alcohols used in the process of the invention.

The primary or secondary monohydric C_1-C_{10} alcohol used in the present invention may in one embodiment be a C_1-C_8 alcohol, such as a C_2-C_5 alcohol, e.g. a C_2-C_4 alcohol, such as a C_3 alcohol. C_x indicates that the alcohol in question has x carbon atoms. Hence, in a further embodiment, the primary or secondary monohydric C_1-C_{10} alcohol is selected from the group consisting of methanol, ethanol, *n*-propanol, isopropyl alcohol, *n*-butanol, *sec*-butanol, isobutyl alcohol, *n*-pentanol, 2-pentanol, 3-pentanol, and mixtures thereof. In another embodiment, the primary or secondary monohydric C_1-C_{10} alcohol is isopropyl alcohol. In yet another embodiment the primary or secondary monohydric C_1-C_{10} alcohol is ethanol.

It should be understood that when referring to "the primary or secondary monohydric C_1-C_{10} alcohol", this also includes mixtures of said alcohols. Thus, in one embodiment, a mixture of two or more primary or secondary monohydric C_1-C_{10} alcohols is used. In another embodiment, only one primary or secondary monohydric C_1-C_{10} alcohol is used. In a particular embodiment, a mixture of isopropyl alcohol and ethanol is used. In a further embodiment, a mixture of isopropyl alcohol and methanol is used.

Molybdenum-based catalyst

The molybdenum-based catalyst employed in the process of the present invention has the formula:

$$A^{q+}{}_a(Mo_vX_xR^1{}_yR^2{}_zR^3{}_e)^{q*a-},$$

wherein

A^{q+} is a mono-, di-, or trivalent counterion;

X is CO, O, OH, S, or Se;

R^1 is selected from the group consisting of H, F, Cl, Br, I, CN, N_3, NCS, dithiocarbamates, CH_3, BF_4, PF_6, SbF_6, and AsF_6;

R^2 is a mono-, bi- or tridentate ligand;

R^3 is a ligand coordinating to the central molybdenum atom through its π system selected from the group consisting of an alkene, a diene, a cyclopentadienyl, methylcyclopentadienyl, or pentamethylcyclopentadienyl radical, benzene, naphthalene, anthracene, or other aromatics;

a is 0, 1, 2, 3, 4, 5, or 6;

v is 1, 2, 3, 4, 5, 6, or 7;

x is in the range 2v to 6v;

y is 0, 1, 2, 3, 4, 5, 6, 7, or 8;

z is 0, 1, 2, or 3; and

e is 0, 1, 2, or 3,

wherein transition metals different from molybdenum are present in a molar amount less than the molar amount of molybdenum.

The element molybdenum can exist in a number of oxidation states from −2 to +6. The molybdenum used in the molybdenum-based catalyst according to the present invention may be in any one of these oxidation states. However, some oxidation states are more frequently encountered than others. Thus, in one embodiment Mo is Mo(IV), Mo(V), or Mo(VI). In another embodiment, Mo is Mo(IV) or Mo(VI), in particular Mo(VI).

The molybdenum-based catalyst may contain a mono-, di-, or trivalent counterion, A^{q+}. This counterion may be selected from the group consisting of simple metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^+, Sn^{2+}, Pb^{2+}, Bi^{3+}, Sc^{3+}, Y^{3+}, Ti^{2+}, Ti^{3+}, V^{2+}, V^{3+}, Cr^{2+}, Cr^{3+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Ru^{2+}, Ru^{3+}, Co^{2+}, Co^{3+}, Rh^{3+}, Ir^{3+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^+, Cu^{2+}, Ag^+, Au^+, Au^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, La^{3+}, and other lanthanides), H^+, NH_4^+, alkyl-substituted ammonium ions, and pyridinium. In one embodiment, A^{q+} is Na^+, NH_4^+, or Bu_4N^+, wherein Bu is butyl.

The X component may be any one of CO, O, OH, S, Se, or mixtures thereof. In one embodiment, X is CO or O. In another embodiment, X is O. In yet another embodiment, X is CO.

R^1 may be selected from any one of H, F, Cl, Br, I, CN, N_3, NCS, dithiocarbamates, CH_3, BF_4, PF_6, SbF_6, and AsF_6, and mixtures thereof. In one embodiment, R^1 is selected from the group consisting of CH_3, Br, Cl, and mixtures thereof. In a further embodiment, R^1 is CH_3. In yet a further embodiment, R^1 is Br. In still a further embodiment, R^1 is Cl.

The R^2 ligand may in principle have any electron pair-donating element as the donor atom. In one embodiment, R^2 has one or more donor atoms selected from the group consisting of N, P, O, and S. In another embodiment, R^2 has one or more nitrogen atoms as donor atoms. In yet another embodiment, R^2 is 2,2'-bipyridine, 1,10-phenanthroline, trispyrazolylborate, ethylenediamine, or $Ph_2PN(R)PPh_2$, wherein Ph is phenyl and wherein R is cyclohexyl, phenyl, or benzyl. In still another embodiment, R^2 is 2,2'-bipyridine. In a further embodiment, R^2 is dimethylsulfoxide (dmso).

The R^2 ligand may be mono-, bi-, or tridentate. In one embodiment, R^2 is a bidentate ligand.

The R^3 ligand may have a hapticity of 2, 3, 5 or 6. It coordinates to the central molybdenum atom through its π system. In one embodiment, R^3 is selected from the group consisting of η^5-cyclopentadienyl, η^5-methylcyclopentadienyl, η^5-pentamethylcyclopentadienyl, η^6-benzene, η^6-toluene, η^6-cymene, η^6-naphthalene, η^6-anthracene, η^3-propenyl.

The value of the various parameters, a, v, x, y, z, and e, may vary. In one embodiment, a is 0, 2, or 6. In another embodiment, v is 1 or 7, in particular 1. The parameter x is in the range 2v to 6v, that is, it may be any integer number in the range 2v to 6v. As an example, if v is 1, then x may be 2, 3, 4, 5, or 6. In one embodiment, x is 2, 4, 6, or 24.

R^1 may be present in the catalyst or it may not be present. Accordingly, y is 0, 1, 2, 3, 4, 5, 6, 7, or 8. In one embodiment, y is 0 or 2. The ligand R^2 may also be absent in the molybdenum-based catalyst. Accordingly, z is 0, 1, 2, or 3. In one embodiment, z is 0 or 1. R^3 may also be absent and is not present in the molybdenum-based catalyst at the same time as R^2. Accordingly, at least one of z and e is 0.

The individual embodiments for each of the parameters a, v, x, y, z, and e, may be combined according to the present invention. Hence, in one further embodiment, a is 0, 2, or 6, v is 1 or 7, x is 2, 4, 6, or 24, y is 0 or 2, z is 0 or 1, and e is 0. Thus, in this embodiment, the molybdenum-based catalyst has the formula:

$$A^{a+}{}_a(Mo_vX_xR^1{}_yR^2{}_z)^{a*a-},$$

wherein

A^{a+} is a mono-, di-, or trivalent counterion;

X is CO, O, OH, S, or Se;

R^1 is selected from the group consisting of H, F, Cl, Br, I, CN, N_3, NCS, dithiocarbamates, CH_3, BF_4, PF_6, SbF_6, and AsF_6;

R^2 is a mono-, bi- or tridentate ligand;

a is 0, 2, or 6;

v is 1 or 7;

x is 2, 4, 6, or 24;

y is 0 or 2; and

z is 0 or 1.

Concrete examples of molybdenum-based catalysts effective in the process of the invention are MoO_2Cl_2(bipy), MoO_2Br_2(bipy), $MoO_2(CH_3)_2$(bipy), $MoO_2Cl_2(dmso)_2$, $(Bu_4N)_2Mo_6O_{19}$, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, wherein bipy is 2,2'-bipyridine, dmso is dimethyl sulfoxide, and Bu is butyl. Accordingly, in one embodiment, the molybdenum-based catalyst is selected from the group consisting of MoO_2Cl_2(bipy), MoO_2Br_2(bipy), $MoO_2(CH_3)_2$(bipy), $MoO_2Cl_2(dmso)_2$, $(Bu_4N)_2Mo_6O_{19}$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and mixtures thereof, wherein bipy is 2,2'-bipyridine, dmso is dimethyl sulfoxide, and Bu is butyl. In a further embodiment,

the molybdenum-based catalyst is selected from the group consisting of $MoO_2(CH_3)_2$(bipy), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(Bu_4N)_2Mo_6O_{19}$, and mixtures thereof, wherein bipy is 2,2'-bipyridine and Bu is butyl. In yet a further embodiment, the molybdenum-based catalyst is $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

The amount of molybdenum-based catalyst used in the process of the invention may vary within a wide range. The amount is balanced by the requirement that enough catalyst is present to catalyze the process on the one hand and the requirement that the process remains economical on the other hand. Accordingly, in one embodiment, the amount of molybdenum-based catalyst is in the range 0.1 to 20 mol%. In another embodiment, the amount of molybdenum-based catalyst is in the range 1 to 15 mol%. In yet another embodiment, the amount of molybdenum-based catalyst is in the range 2 to 10 mol%. In still another embodiment, the amount of molybdenum-based catalyst is in the range 3 to 8 mol%. In a further embodiment, the amount of molybdenum-based catalyst is in the range 4 to 7 mol%, such as approximately 5 mol%.

The molar amount of transition metals different from molybdenum present in the molybdenum-based catalyst according to the invention is less than the molar amount of molybdenum. When referring to the "molar amount of transition metals different from molybdenum", it means the combined molar amounts of all transition metals different from molybdenum. In one embodiment, the molar amount of transition metals different from molybdenum is 50% or less of the molar amount of molybdenum. In another embodiment, the molar amount of transition metals different from molybdenum is 40% or less of the molar amount of molybdenum. In yet another embodiment, the molar amount of transition metals different from molybdenum is 30% or less of the molar amount of molybdenum. In still another embodiment, the molar amount of transition metals different from molybdenum is 20% or less of the molar amount of molybdenum. In a further embodiment, the molar amount of transition metals different from molybdenum is 10% or less of the molar amount of molybdenum. In yet a further embodiment, the molar amount of transition metals different from molybdenum is 5% or less of the molar amount of molybdenum. In still a further embodiment, the molar amount of transition metals different from molybdenum is 2% or less of the molar amount of molybdenum.

Solvent

The primary or secondary monohydric C_1-C_{10} alcohol acting as reductant in the process according to the present invention may also conveniently act as a solvent. Hence, the process may be carried out with or without an additional solvent. Accordingly, in one embodiment the process is carried out without a solvent in addition to the primary or secondary monohydric C_1-C_{10} alcohol. In a further embodiment, the process is carried out in a further solvent different from and in addition to the primary or secondary monohydric C_1-C_{10} alcohol.

If an additional solvent is used, it should preferably be chosen so that the solubility of the polyol and the molybdenum-based catalyst is high enough to fully dissolve both these components. Suitable solvents for the process of the present invention include 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, diglyme, triglyme, tetraglyme, diethyleneglycol, triethyleneglycol, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, triacetin, dimethyl sulfoxide, acetone, tetrahydrofuran, tetrahydropyran, oxepane, dimethyl ether, diethyl ether, diisoproyl ether, dipropyl ether, dibutyl ether, acetaldehyde diethyl acetal, or mixtures thereof.

The product

Depending on the exact reaction conditions, the product of the process may vary. In one embodiment, the resulting product of the process according to the present invention having the highest molar percentage is the compound corresponding to the polyol wherein at least one α,β-dihydroxyl group has been converted into an α,β-carbon–carbon double bond.

An example of the latter is when the polyol has at least three adjacent hydroxyl groups and is converted into the corresponding allylic alcohol. Hence, in a further embodiment, the resulting product of the process according to the invention having the highest molar percentage is the allylic alcohol corresponding to a polyol having at least three adjacent hydroxyl groups. In yet a further embodiment the polyol is glycerol and it is converted into allyl alcohol. The allyl

alcohol may under some circumstances of the process of the invention be reduced further to propylene. Hence, in still a further embodiment, the polyol is glycerol and it is converted into a mixture of allyl alcohol and propylene. In still another embodiment, the polyol is glycerol and it is converted into propylene.

Addition of a base

It has been found that in some embodiments the addition of a base increases the yield of the product wherein at least one α,β-dihydroxyl group has been converted into an α,β-carbon–carbon double bond. Hence, in one embodiment the process of the invention includes the addition of a base. In another embodiment, said base is soluble in the primary or secondary monohydric C_1-C_{10} alcohol used in the present invention.

Examples of bases soluble in the primary or secondary monohydric C_1-C_{10} alcohol used in the present invention include tetrabutylammonium hydroxide (Bu_4NOH) and other quaternary ammonium hydroxides. Hence, in a further embodiment the base is a quaternary ammonium hydroxide, such as a base selected from the group consisting of tetrabutylammonium hydroxide, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetramethylammonium hydroxide, and mixtures thereof. In still a further embodiment, the base is tetrabutylammonium hydroxide (Bu_4NOH). Other examples of suitable bases include carbonates, acetates, pyridine, and triethylamine.

Additional embodiments

The inventors of the present invention have found that the yield does not depend significantly on whether it is carried out under an inert atmosphere or not. However, circumstances may dictate that an inert atmosphere is used. Thus, in one embodiment, the process is carried out under an inert atmosphere.

Examples

Example 1 – Deoxydehydration of 1,2-decanediol

In the following examples, unless something else is stated, 40 mmol of diol, 2.0 mmol of catalyst (5 mol%, calculated with respect to the amount of molybdenum), 500 mg of hexadecane (internal standard), and 100 ml of solvent were mixed in a 300 ml PTFE cup and placed in a 400 ml autoclave with a magnetic stir bar and computer-controlled heating plate. The autoclave was sealed, pressurized with 10–25 bar of H_2 or N_2, and heated to 250 °C for 800 min (corresponding to ~12 h at the reaction temperature); the temperature typically stabilized between 240 and 250 °C, while the maximum pressure was 60–90 bar. When the system had cooled to room temperature, the pressure was released, the reaction mixture was filtered to remove a fine, black precipitate and analyzed by GC (for determination of conversion and yields) and GC-MS (for observation and identification of other products).

Comparison of solvents

A number of primary or secondary monohydric C_1-C_{10} alcohol solvents were tested together with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as the catalyst. In addition, their performance was compared to that of tertbutyl alcohol, acetone, and hexane as solvents. The yields of 1-decene (**C=C**), 2-decanone (**C=O**), 2-decanol (**2°OH**), and 1-decanol (**1°OH**) are provided below in Table 1.

It is evident that using a primary or secondary monohydric C_1-C_{10} alcohol as the solvent results in a better selectivity of reduced products than any of the comparative solvents.

Table 1 – Comparison of organic solvents in the deoxydehydration of 1,2-decanediol using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as the catalyst.[a]

Solvent	T_{max} [°C]	p_{max} [bar]	Conv. [%]	Yields [%]			
				C=C	**C=O**	**2°OH**	**1°OH**
MeOH[b]	239	85	57	17	5	<1	2
EtOH	247	78	full	37	11	5	10
*n*PrOH	251	70	full	36	13	7	11
*i*PrOH	242	61	full	49	10	5	15
1-Butanol[e]	253	46	full	15	10	6	11
2-Butanol[e]	253	54	full	40	11	3	16
1-Pentanol[e]	254	38	full	12	[f]	[f]	[f]
3-Pentanol	252	55	full	33	8	5	14
*t*BuOH[c],[d]	232	103	39	~0	~0	~0	~0
Acetone[d]	249	74	96	11	23	1	~0
Hexane[d]	247	65	full	31	17	2	5

[a] Standard reaction conditions were employed unless otherwise noted; the autoclave was pressurized with hydrogen unless otherwise noted. [b] Heated for 900 min. [c] Heating stopped after 350 min, because dehydration of *t*BuOH to isobutylene resulted in a rapidly increasing pressure. [d] Comparative examples. [e] The autoclave was pressurized with 15 bar of nitrogen. [f] Due to overlap with other compounds on the GC, the yields could not be determined.

Example 2 – The influence of the gas phase

In order to exclude the possibility in Example 1 that hydrogen acted as a reductant, a comparison was made with nitrogen instead of hydrogen. Using the same reaction conditions as in Example 1, including the $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ catalyst, the results are summarized in Table 2 below. It is evident that the hydrogen gas does not act as a reductant during the reaction.

Table 2 - Comparison of hydrogen and nitrogen gas in the deoxydehydration of 1,2-decanediol in the solvents hexane and *i*PrOH using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as the catalyst.

Gas	Solvent	T_{max} [°C]	p_{max} [bar]	Yields [%] of			
				C=C	**C=O**	**2° OH**	**1° OH**
22 bar of H_2	Hexane	247	65	31	17	2	5
10 bar of N_2	Hexane	246	44	30	19	3	4
15 bar of H_2	*i*PrOH	242	61	49	10	5	15
10 bar of N_2	*i*PrOH	242	63	46	10	6	13

Example 3 – Varying the molybdenum-based catalyst

In addition to ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, a number of other oxomolybdenum-based catalysts were tested. The results are summarized in Table 3.

The addition of base in the form of a methanolic solution of Bu_4NOH improves the alkene yield as well as the total yield of reduced species.

Table 3 – Test of molybdenum-based catalysts in the deoxydehydration of 1,2-decanediol in *i*PrOH.[a]

Catalyst	Conv. [%]	Yields [%] of			
		C=C	**C=O**	**2°OH**	**1°OH**
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	full	49	10	5	15
$MoO_2Cl_2(dmso)_2$[b]	98	23	9	3	27
$MoO_2(CH_3)_2(bipy)$[c]	89	46	11	3	12
$MoO_2Cl_2(bipy)$[c]	full	31	10	~0	2
$MoO_2Br_2(bipy)$[c]	full	15	6	~0	2
$H_3PMo_{12}O_{40}\cdot xH_2O$	98	20	7	3	21
$(Bu_4N)_2Mo_6O_{19}$	full	42	8	9	23
$MoO_3\cdot H_2O$	96	34	11	4	22
$(NH_4)_6MnMo_9O_{32}\cdot 8H_2O$	full	47	7	5	16
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ + base[d]	full	55	~0	22	3
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ + acid[e]	92	37	8	3	11
Mo(s)[f]	17	7	1	~0	1

[a] Standard reaction conditions were employed (as in Example 1). [b] dmso = dimethyl sulfoxide. [c] bipy = 2,2′-bipyridine. [d] Six milliliters of a 1 M solution of Bu_4NOH in MeOH was added. [e] Acetic acid (1.2 equiv with respect to 1,2-decanediol) was added to the reaction mixture; 92% conversion. [f] Comparative example: Molybdenum powder (<150 µm, 99.9%) purchased from Sigma-Aldrich, product number 266892.

Example 4 – Variations in reaction conditions

The effects of changing catalyst loading, diol loading, reaction time, and temperature were screened. The results are summarized in Table 4 below.

A shorter reaction time of only 400 min (entry 2) resulted in an incomplete conversion, and although a higher catalyst loading of 13 mol% (entry 3) gave full conversion within 400 min, the alkene yield was not improved and the total yield was slightly lower.

Lowering the concentration of the catalyst (using $(Bu_4N)_2Mo_6O_{19}$ instead of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as the former is more stable) from 5 to 1 mol% (entries 6 and 7) and concurrently increasing the reaction time to ~60 h resulted in an almost full conversion but a slightly lower alkene yield. The control experiment without any catalyst at all (entry 5) resulted in only traces of alkene and none of the other products.

Lowering the concentration of the diol to only 18 mmol (entry 4) did not affect the yields significantly. Lowering the reaction temperature to <230 °C resulted in 63 and 87% conversion after 900 and 1440 min, respectively (entries 8 and 9); the selectivity was not altered.

Table 4 – Variations in reaction conditions for the molybdenum-catalyzed deoxydehydration of 1,2-decanediol in *i*PrOH.

Entry	x_{Mo}	t	T_{max}	Conv.	Yields [%]			
	[mol%]	[min]	[°C]	[%]	**C=C**	**C=O**	**2°OH**	**1°OH**
1	5.0	800	240	full	49	10	5	15
2	4.8	400	240	83	42	9	3	12
3	13	400	240	98	50	8	3	11
4	4.8[a]	800	237	96	52[b]	7	4	13
5	0	800	240	n.d.	2	~0	~0	~0
6	5.0[c]	800	243	full	42	8	9	23
7	1.1[c]	3680	246	98	35[d]	10	8	24
8	4.6	900	228	63	32	6	2	9
9	4.8	1440	227	87	44	8	4	12

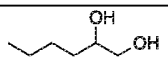
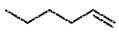
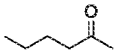
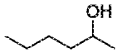
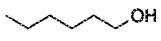
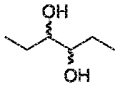
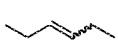
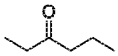
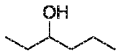
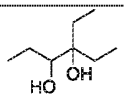
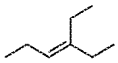
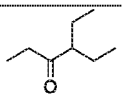
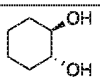
Abbreviations: **C=C** 1-decene, **C=O** 2-decanone, **2°OH** 2-decanol, **1°OH** 1-decanol. [a] Only 18 mmol of diol was added. [b] Includes 39% 1-decene and 13% isomers of decene and decane. [c] The catalyst was $(Bu_4N)_2Mo_6O_{19}$ instead of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. [d] Includes 30% 1-decene and 5% isomers of decene and decane.

Example 5 – Variations in the polyols

The process according to the invention works for a variety of different polyols. The results for a number of aliphatic diols containing combinations of primary, secondary, and tertiary OH groups are compiled in Table 5 below.

The product yields and distributions from the 3,4-hexanediol (a diol containing two secondary OH groups) were similar to those from 1,2-hexanediol (a diol containing a primary and a secondary OH group). The diol 3-ethyl-3,4-hexanediol, which contains a secondary and a tertiary OH group, underwent cleavage to 3-pentanol/3-pentanone (combined yield 57%; interconverted through transfer hydrogenation) and presumably 1-propanol/propanal, although the latter was not unequivocally observed by GC-MS due to interference with 2-propanol/acetone. The primary reaction for 2-ethyl-1,2-butanediol was not cleavage but dehydration and transfer hydrogenation to form the primary alcohol 2-ethyl-1-butanol (69%). Pinacol, which contains two tertiary OH groups, was transformed into 28% of alkene and 4% of pinacolone (by pinacol rearrangement).

Table 5. Reactivity of aliphatic diols.[a]

Polyol	Yields [%]			
				
1,2-hexanediol	46%	9%	traces	16%
				
3,4-hexanediol	42%[b]	17%	5%	
				
2-ethyl-1,2-butanediol	unknown[c]	69%	unknown[c]	
				
3-ethyl-3,4-hexanediol	25%	4%	42%	15%
				
pinacol	28%	4%		
				
cis-1,2-cyclohexanediol	29	traces	42	
				
trans-1,2-cyclohexanediol[d]	14	4	24	

[a] The reactions were conducted on 20 mmol scale in 50 ml of *i*PrOH in pressurized Swagelok cylinders heated to 240–250 °C for 18 h. [b] Mixture of isomers; calculation of 3-hexene yield was complicated by overlap with iPr_2O. [c] Due to overlap with iPr_2O, the yields of the three C_6H_{12} isomers could not be determined accurately; the total yield was estimated to be 20%. [d] Conversion was incomplete.

Example 6 – The effect of base.

Addition of base to the reaction mixture was shown in Example 3 to be beneficial and was investigated further. Addition of 15 mol% of base (Bu_4NOH) dissolved in MeOH improved the alkene yield significantly. For *cis*-1,2-cyclohexanediol, the yield of cyclohexanol was still high, but the combined yield of reduced species was 92%.

Table 6. Comparison of the deoxydehydration of various C_6 diols in *i*PrOH catalyzed by $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.[a]

Polyol	Yields [%]			
	C=C	**C=O**	**2°OH**	**1°OH**
1,2-hexanediol	46	9	traces	16
+ 3 ml of MeOH	49	15	3	11
+ 3 mmol of Bu_4NOH[b]	77	3	5	5
+ 3 mmol of pyridine[c]	42	15	13	15
cis-1,2-cyclohexanediol	29	traces	42	
+ 3 mmol of Bu_4NOH[b]	47	traces	45[d]	

[a] Reactions conducted in Swagelok cylinders using 20 mmol of diol, 50 ml of *i*PrOH, and 5 mol% of ammonium heptamolybdate and heating to 240–250 °C for 18 h under 15 bar of N_2. Unless otherwise noted, the conversion of the diol was >98%. Abbreviations: **C=C** 1-hexene or cyclohexene, **C=O** 2-hexanone or cyclohexanone, **2°OH** 2-hexanol or cyclohexanol, **1°OH** 1-hexanol. [b] Three milliliters of 1 M Bu_4NOH in MeOH was added. [c] Dissolved in 3 ml of MeOH. [d] Based on GC-MS due to partial overlap with Bu_3N on the GC.

Example 7 – Reduction of glycerol

The ammonium heptamolybdate-catalyzed deoxydehydration of glycerol in *i*PrOH was attempted using the reaction conditions specified in Example 1 and adding 15 mol% of base (1 M Bu_4NOH in MeOH), with the following modifications:
The reactions were conducted on half scale in a 100 ml Swagelok cylinder, which for 18 h was placed in an aluminum block that had been preheated to 250 °C.

The conversion was complete, and in addition to 4% of allyl alcohol and traces of 1,5-hexadiene, 19% of propylene was quantified. In EtOH, the conversion was also complete, and in addition to traces of allyl alcohol and 1,5-hexadiene, 9% of propylene was quantified.

The quantification method for propylene was not optimized and it is believed that the actual amount of propylene formed in the reaction is significantly higher than the measured amount.

Example 8 – Reduction of allyl alcohol

A mixture of 70 mmol of allyl alcohol, 1.4 mol% of ammonium heptamolybdate and 4.2 mol% of base (1 M Bu_4NOH in MeOH) in 50 ml of *i*PrOH was heated to 250 °C for 18 h (conditions as in Example 7), which led to the formation of 8% of 1,5-hexadiene and 22% of propylene; the conversion was 86%. In EtOH, the yields were 9% and 28%, respectively, while the conversion was 86%.

The quantification method for propylene was not optimized and it is believed that the actual amount of propylene formed in the reaction is significantly higher than the measured amount.

Example 9 – Reduction of erythritol

The ammonium heptamolybdate-catalyzed deoxydehydration of erythritol in *i*PrOH was attempted using the reaction conditions specified in Example 1, with the following modifications: The reactions were conducted on half scale in a 100 ml Swagelok cylinder, which for 18 h was placed in an aluminum block that had been preheated to 250 °C. The conversion was complete, and 39% of 2,5-dihydrofuran formed.

Example 10 – Reduction of 1,4-anhydroerythritol

The ammonium heptamolybdate-catalyzed deoxydehydration of 1,4-anhydroerythritol in *i*PrOH was attempted using the reaction conditions specified in Example 1, with the following modifications: The reactions were conducted on half scale in a 100 ml Swagelok cylinder, which for 18 h was placed in an aluminum block that had been preheated to 250 °C. The conversion was complete, and 75% of 2,5-dihydrofuran formed.

Claims

1. A process for the reduction of a polyol wherein at least two of the hydroxyl groups are located on adjacent carbon atoms comprising the reaction of the polyol with a primary or secondary monohydric C_1-C_4 alcohol in the presence of a molybdenum-based catalyst at a temperature of at least 175 °C, wherein said molybdenum-based catalyst has the formula:

$$A^{q+}{}_a(Mo_vX_xR^1{}_yR^2{}_zR^3{}_e)^{q*a-},$$

wherein

A^{q+} is a mono-, di-, or trivalent counterion;

X is CO, O, OH, S, or Se;

R^1 is selected from the group consisting of H, F, Cl, Br, I, CN, N_3, NCS, dithiocarbamates, CH_3, BF_4, PF_6, SbF_6, and AsF_6;

R^2 is a mono-, bi- or tridentate ligand;

R^3 is a ligand coordinating to the central molybdenum atom through its π system selected from the group consisting of an alkene, a diene, a cyclopentadienyl, methylcyclopentadienyl, or pentamethylcyclopentadienyl radical, benzene, naphthalene, anthracene, or other aromatics;

a is 0, 1, 2, 3, 4, 5, or 6;

v is 1, 2, 3, 4, 5, 6, or 7;

x is in the range 2v to 6v;

y is 0, 1, 2, 3, 4, 5, 6, 7, or 8;

z is 0, 1, 2, or 3; and

e is 0, 1, 2, or 3, such as 0,

wherein transition metals different from molybdenum are present in a molar amount less than the molar amount of molybdenum, and

wherein said polyol and said molybdenum-based catalyst are dissolved in said primary or secondary monohydric C_1-C_4 alcohol or wherein said polyol, said molybdenum-based catalyst, and said primary or secondary monohydric C_1-C_4 alcohol are dissolved in an additional solvent.

2. The process according to claim 1, wherein the temperature is in the range 175 to 300 °C, such as in the range 190 to 290 °C, e.g. in the range 200 to 280 °C,

preferably in the range 220 to 270 °C, even more preferably in the range 230 to 260 °C.

3. The process according to any one of the preceding claims, wherein the polyol is selected from the group consisting of 1,2-hexanediol, 3,4-hexanediol, *cis*-1,2-cyclohexanediol, 1,2-decanediol, and glycerol.

4. The process according to claim 3, wherein the polyol is glycerol.

5. The process according to any one of the preceding claims, wherein the polyol and the molybdenum-based catalyst are dissolved in said primary or secondary monohydric C_1-C_4 alcohol.

6. The process according to any one of the preceding claims, wherein the primary or secondary monohydric C_1-C_4 alcohol, is a C_2-C_4 alcohol, such as a C_3 alcohol.

7. The process according to claim 6, wherein the primary or secondary monohydric C_1-C_4 alcohol is selected from the group consisting of methanol, ethanol, *n*-propanol, isopropyl alcohol, and mixtures thereof; in particular isopropyl alcohol or ethanol, preferably isopropyl alcohol.

8. The process according to any one of the preceding claims, wherein the amount of molybdenum-based catalyst is in the range 0.1 to 20 mol%, such as in the range 1 to 15 mol%, e.g. in the range 2 to 10 mol%, preferably in the range 3 to 8 mol%, more preferably in the range 4 to 7 mol%.

9. The process according to any one of the preceding claims, wherein A^{q+} is absent or NH_4^+.

10. The process according to claim 9, wherein R^2 is 2,2'-bipyridine or dimethyl sulfoxide, in particular 2,2'-bipyridine.

11. The process according to any one of the preceding claims, wherein v is 1 or 7.

12. The process according to any one of the preceding claims, wherein a is 0, 2, or 6.

13. The process according to any one of the preceding claims, wherein the molybdenum-based catalyst is selected from the group consisting of MoO_2Cl_2(bipy), MoO_2Br_2(bipy), $MoO_2(CH_3)_2$(bipy), MoO_2Cl_2(dmso)$_2$, $(Bu_4N)_2Mo_6O_{19}$, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and mixtures thereof, wherein bipy is 2,2'-bipyridine; in particular $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

14. The process according to any one of the preceding claims, wherein the molybdenum-based catalyst is $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and the primary or secondary monohydric C_1-C_{10} alcohol is isopropyl alcohol.

15. The process according to any one of the preceding claims, wherein the process is carried out in the presence of a base.

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2015/050359

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C1/22 C07C11/02 C07C11/06 C07C11/107 C07C11/113
C07C11/12 C07C13/20 C07C29/60 C07C31/125 C07C35/08
C07C45/52 C07C49/04 C07C49/403 C07D307/28 B01J23/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C C07D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DETHLEFSEN, J.R. ET AL.: "Molybdenum-Catalyzed Deoxydehydration of Vicinal Diols", CHEMSUSCHEM, vol. 7, no. 2, 7 January 2014 (2014-01-07) , pages 425-428, XP055174860, ISSN: 1864-5631, DOI: 10.1002/cssc.201300945 cited in the application	1-13,15
A	the whole document	14
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2016	22/02/2016

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2015/050359

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SHIRAMIZU, M. ET AL.: "Expanding the Scope of Biomass-Derived Chemicals through Tandem Reactions Based on Oxorhenium-Catalyzed Deoxydehydration", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 52, no. 49, 12 November 2013 (2013-11-12), pages 12905-12909, XP55173628, ISSN: 1433-7851, DOI: 10.1002/anie.201307564	1-13,15
A	page 12905, column 1 page 12906; table 1	14

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Y	ARCEO, E. ET AL.: "Rhenium-Catalyzed Didehydroxylation of Vicinal Diols to Alkenes Using a Simple Alcohol as a Reducing Agent", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 132, no. 33, 29 July 2010 (2010-07-29), pages 11408-11409, XP055086386, ISSN: 0002-7863, DOI: 10.1021/ja103436v cited in the application	1-13,15
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A	the whole document	14

Y,P	WO 2015/028028 A1 (DANMARKS TEKNISKE UNIVERSITET) 5 March 2015 (2015-03-05)	1-13,15
A,P	abstract; claims; examples page 12, last paragraph	14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/DK2015/050359

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015028028 A1	05-03-2015	NONE	